BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1134—1136 (1973)

Study of the Poisoning Effect on Nickel and Nickel Boride Catalysts by Means of a Flow Microcalorimeter

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(Received July 5, 1972)

The relation between the poisoning effect on nickel and nickel boride catalysts in the liquid-phase hydrogenation of styrene and the bond strength of inhibitors on the catalysts has been studied by means of liquid-phase chromatography using a thermal detector. The results show that the sequence of poisoning effect is in agreement with that of the adsorption heat of inhibitors, and that the adsorption heat of each inhibitor on nickel boride is smaller than that on nickel. Besides, this sequence is also in agreement with that of the bond strength of the central metal ion and the coordinated ligand of some manganese complexes in a homogeneous system. These facts indicate that the adsorption energy of inhibitors on a catalyst in a heterogeneous system corresponds to the bond strength of the ligand coordinated to metal complexes in a homogeneous system.

The poisoning effect on nickel and nickel boride catalysts in the liquid-phase hydrogenation of styrene has mainly been studied by the kinetic method, and it has previously been reported that the resistibility of the nickel boride catalyst was greater than that of the nickel catalyst.[1]

Since the poisoning effect is assumed to be connected with the bond strength between a catalyst and an inhibitor, the adsorption heat of the inhibitor was measured by means of liquid-phase chromatography using a thermal detector.

The results showed that the sequence of the poisoning effect was in agreement with that of the adsorption heats of inhibitors on the catalysts. Besides, the resistibility to inhibition on nickel and nickel boride catalysts was also studied in relation to the adsorption heats of inhibitors on the catalysts. Each adsorption heat of inhibitor on nickel boride was smaller than that on nickel; accordingly, nickel boride can be said to exhibit a higher resistibility than that of nickel. Furthermore, the sequence of the poisoning coefficient estimated by taking the steric effect into account was in agreement with that of the bond strength of adsorption obtained with the thermal measurements; this sequence was also in agreement with that of the bond strength between the central metal ion and the ligand coordinated to some manganese complexes[2] in a homogeneous system.

Experimental

Materials. The Ni_2B catalyst was prepared by adding $NaBH_4$ to a solution of $(CH_3COO)_2Ni$ ($Ni=0.6$ g), as has been desdribed in the previous publication;[1] the precipitate was washed and centrifuged with ethanol. The BET surface area of the Ni_2B catalyst was 21.8 m^2/g. The Ni catalyst used was degassed by heating $(HCOO)_2Ni$ at about 250°C for 3—4 hr under a vacuum and cooled after charging in hydrogen gas; then ethanol was poured into the reaction vessel. The BET surface area of this Ni catalyst was 13.8 m^2/g.

The dichlorophenyl phosphine, trialkyl phosphites, and 2,3-dimercaptopropanol were used without further purification. The styrene was purified by distillation before use.

Procedures. The apparatus used for the thermal measurements is shown schematically in Fig. 1. The catalyst prepared was charged in the columns of both the detector and reference parts. In order to remove the oxygen soluted in the carrier liquid (99.5% ethanol), the hydrogen was saturated by bubbling it through the gas-adsorption vessel. Stable thermal measurements were made possible by this procedure. The inhibitors were injected into the carrier liquid from the inlet part as an ethanol solution of a certain

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[1] Y. Nitta, T. Imanaka, and S. Teranishi, *Kogyo Kagaku Zasshi*, **74**, 777 (1971).

[2] R. J. Angelici and F. Basolos, *J. Amer. Chem. Soc.*, **84**, 2475 (1962).

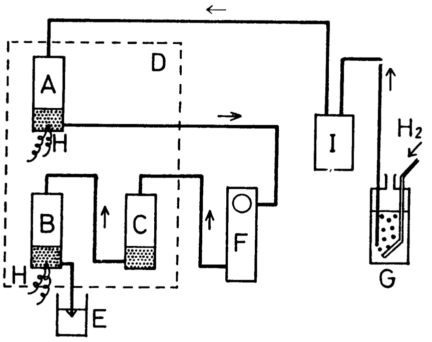

Fig. 1. Block diagram of the apparatus used.

A: Reference column, B: Detector column, C: Adsorption column, D: Water bath, E: Recovery vessel, F: Sample inlet, G: Hydrogen Saturator, H: Thermistor, I: Pump. Eluent: 99.5% ethanol, Flow rate: 0.62 ml/min, Pressure: 2—3 kg/cm^2, Temperature of the water bath: 35°C.

concentration of the inhibitor.

The exothermic value calculated from the peak area per unit of the catalyst was determined by means of liquid chromatography using a thermal detector (NIHON Electric Company, JLC-A). First, the heats of adsorption of inhibitors per unit of catalyst were determined against the amounts of inhibitors injected, without the adsorption column (C). Second, the amounts of injected inhibitors adsorbed by the catalyst in the detector column (B) were estimated by determining the heat effects produced by the same inhibitors after they had left an identical column (C), filled with the same catalyst and connected in series between the sample injection part (F) and the detector column (B). Since the residual inhibitor passing through the first column (C) subsequently entered the detector column (B) and produced a heat effect similar to those produced by the inhibitors injected directly, the amount of that inhibitor was obtained from the relations, determined previously, between different amounts of the inhibitors injected directly and the heat effects they produce.

Thus, the quantity of inhibitor adsorbed in the first column was determined by subtracting the amount obtained above from that of the inhibitor injected.[3] However, the adsorption heat of the inhibitor was corrected by subtracting the heat of dilution of the sample solution with ethanol.

The measurements of the rate of hydrogenation reaction were performed directly in the usual manner[4] at 30°C, using 1 ml of styrene as a reactant and 40 ml of ethanol as a solvent. In order to eliminate the change in catalytic activity arising from the preparation of the catalyst, the rate of hydrogenation on the catalyst without any inhibitor was at first measured using 1 ml of styrene. When the reaction was complete, the inhibitor was added to the reaction mixture; it was stirred for 10 min, and then the rate of hydrogenation was again measured by adding 1 ml of styrene. As the hydrogenation reaction proceed in zero-order in the styrene concentration, the rate of hydrogen uptake was used as the hydrogenation rate when 50% of the added styrene had been hydrogenated to ethylbenzene.

The catalytic activity was determined by means of the ratio of the hydrogenation rate on the catalyst with and without an inhibitor. In this case, it was confirmed that the catalyst was not poisoned with styrene or ethylbenzene, a hydrogenated substance, and that the activity of the catalyst without an inhibitor did not change with a repetition in the reaction.

Results and Discussion

The relation between the exothermic value of trimethylphosphite, P(OMe)$_3$, as an inhibitor and the amount of inhibitor added to nickel and nickel boride catalysts is shown in Fig. 2. In these catalysts, the exothermic values are proportional to the amounts of several inhibitors. Figure 3 shows the amount of inhibitor added against the amount of triphenylphosphite, P(Oph)$_3$, adsorbed per unit of catalyst when the adsorption column is connected in series to the sample column. It was found that the amount of adsorption increases with an increase in the amount of inhibitor added. The fact that the amount of adsorption on nickel boride is more than that on nickel may be due to the difference in the surface areas of the catalysts. Table 1 shows the adsorption heats of several inhibitors on nickel and nickel boride catalysts against the modified poisoning coefficients, α'[1,5], calculated from the poisoning coefficients, α,

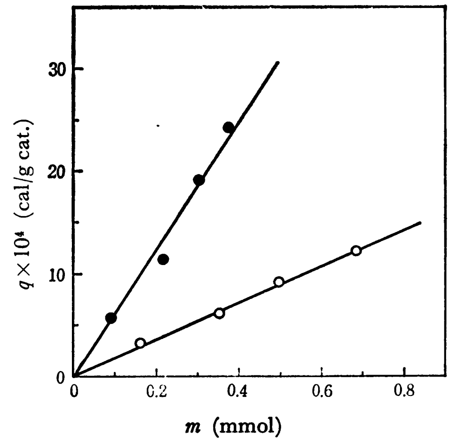

Fig. 2. Relation between exothermic value and the amount of added inhibitor.

○: Ni$_2$B, ●: Ni

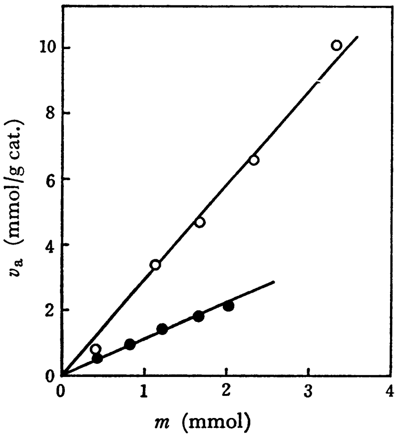

Fig. 3. Relation between the amount of adsorption and the amount of added inhibitor.

○: Ni$_2$B, ●: Ni

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[3] A. J. Groszek, *ASLE Transactions*, **5**, 105 (1962).

[4] Y. Murakami, S. Kishida, T. Imanaka, and S. Teranishi, *Nippon Kagaku Zasshi*, **89**, 263 (1968).

[5] $\alpha'=\alpha/s$, s; the occupied area of adsorbed inhibitor molecule (Å^2).

Table 1. Heat of adsorption and poisoning coefficient of several inhibitors

Inhibitor	Catalysts			
	Ni_2B		Ni	
	Heat of adsorp. (cal/mol)	Poisoning coeff. (gNi/mmol, Å^2)	Heat of adsorp. (cal/mol)	Poisoning coeff. (gNi/mmol, Å^2)
$CH_2(SH)CH(SH)CH_2OH$	84.2	0.169	104	1.41
$PPhCl_2$	124	0.341	142	1.73
$P(OCH_3)_3$	0.610		5.72	0.695
$P(OPh)_3$	0.332		4.31	0.203
$P(On\text{-}Bu)_3$	0.317		3.34	0.163

of the Maxted equation[6] $K_c=K_0(1-\alpha C)$, obtained from the hydrogenation rate of styrene [K_c, K_0; activity with or without an inhibitor, C; amount of added inhibitor(mmol/gNi)]. As has been shown in the preceding paper,[1] it was also found by means of thermal measurements that the resistibility to the inhibitor of nickel boride is more than that of nickel. The high resistibility to the poisoning of the nickel boride catalyst is probably due to the effect that the bonding electrons of the boron atom occupy the vacant d-orbitals of the nickel atom and make it difficult for the lone pairs of the inhibitors to coordinate with and so poison the nickel catalyst. Furthermore, the sequence of the poisoning coefficients for nickel and nickel boride catalysts was as follows;

$$PPhCl_2 > CH_2(SH)CH(SH)CH_2OH > P(OCH_3)_3 > P(OPh)_3 > P(On\text{-}Bu)_3$$

In addition, the sequence of the adsorption heats of inhibitors for nickel and nickel boride catalysts obtained from the thermal measurements agrees completely with the preceding sequence; therefore, it was found that the poisoning coefficient for a catalyst is subject to the bond strength of the adsorption of the inhibitor.

It has previously been reported that the infrared spectra of some $Mn(CO)_4LX$ (X=Cl, Br, I)[2] complexes in the CO stretching region show an increase in the wave number of adsorption with the changes in L in this sequence:

$$P(C_6H_5)Cl_2 \geq P(OCH_2)_3CCH_3 > P(OC_6H_5)_3 \geq P(OC_4H_9)_3 > Sb(C_4H_9)_3 \sim As(C_6H_5)_3 \sim P(C_6H_5)_3 > P(C_4H_9)_3$$

When styrene is used as the ligand of the manganese complex, it can be considered that the electron-attracting ability of styrene is weaker than that of the $P(C_4H_9)_3$ ligand.

The increase in the wave number of the C–O absorption suggests that the strong electron-attracting ligand results in less electron density on manganese, which means less back-donation of the d-orbital electron and, therefore, less Mn–C bond strength. The sequence of increase along the $P(C_6H_5)Cl_2 \gg P(OC_6H_5)_3 > P(OC_4H_9)_3$ series agrees completely with the sequence of the poisoning coefficients for nickel and nickel boride catalysts, as is shown in Table 1. This fact indicates that the magnitude of the adsorption energy of inhibitors on a catalyst in a heterogeneous system corresponds to the bond strength of the ligand coordinated to metal complexes in a homogeneous system.

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[6] E. B. Maxted, *Advan. Catal.*, **3**, 129 (1951).